JOURNAL OF APPLIED POLYMER SCIENCE VOL. 16, PP. 2835–2845 (1972)

Graft Copolymers of Starch with Mixtures of Acrylamide and the Nitric Acid Salt of Dimethylaminoethyl Methacrylate

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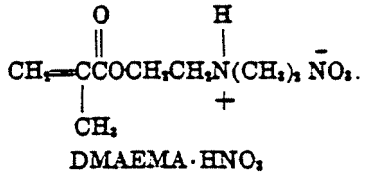
Synopsis

Mixtures of acrylamide and the nitric acid salt of dimethylaminoethyl methacrylate (DMAEMA·HNO_3) have been graft polymerized onto unmodified wheat starch with ferrous ammonium sulfate–hydrogen peroxide initiation. Graft polymerizations were carried out with both unswollen starch granules and granules that had been swollen by heating in water to 60°C. Ungrafted synthetic polymers were removed from graft copolymers by cold-water extraction and were characterized by their $\bar{M}_n$ and DMAEMA·HNO_3 content. Graft copolymers were characterized with respect to per cent add-on, $\bar{M}_n$ and DMAEMA·HNO_3 content of grafted polymer, and grafting frequency. Ungrafted synthetic polymers contained a mole percentage of DMAEMA·HNO_3 equal to or greater than that present in the initial monomer mixtures; whereas in most grafted polymers the mole-% DMAEMA·HNO_3 in the grafted branches was less than that in the starting monomers. At all monomer ratios examined, polymer grafted to swollen starch granules contained a higher percentage of DMAEMA·HNO_3 then polymer grafted to unswollen starch. The influence of starch granule swelling on the molecular weight and frequency of grafted branches was correlated with the composition of the initial monomer mixture. It was determined that the effect of granule swelling on graft copolymer structure would be minimal when 25–30 mole-% DMAEMA·HNO_3 was used. In an acetonitrile–water solvent system, reactions with 20 and 50 mole-% DMAEMA·HNO_3 produced graft copolymers with less DMAEMA·HNO_3 in grafted branches than corresponding graft polymerizations run in water. The flocculation of 3% aqueous suspensions of diatomaceous silica was examined with selected starch graft copolymers.

INTRODUCTION

Previously, we had prepared and characterized graft copolymers of starch with the nitric acid salt of dimethylaminoethyl methacrylate (DMAEMA·HNO_3), as well as tested them as flocculating agents[1]:



DMAEMA·HNO_3

As a further step in our research on cationic starch graft copolymers, we have now prepared and characterized starch graft copolymers from mixed monomer systems containing varying proportions of DMAEMA·HNO_3 and acrylamide. Acrylamide was chosen as a comonomer since it gives a water-soluble polymer and is the major component of a number of commercially available flocculants.

Compared with single monomer grafting, little research has been published on the synthesis and characterization of starch graft copolymers from mixed monomer systems. We determined the percentages of cationic monomer incorporated in both grafted and ungrafted synthetic polymers at various initial mole percentages of DMAEMA·HNO_3. Also, we show that starch granule swelling markedly influences the DMAEMA·HNO_3 content of grafted branches at all initial monomer ratios. Graft molecular weights and grafting frequencies were determined for all graft copolymers, and the behavior of selected graft copolymers as flocculants was examined.

EXPERIMENTAL

Materials

Unmodified wheat starch (Huron Starbake) was purchased from Hercules Inc.

Ferrous ammonium sulfate hexahydrate and 50% hydrogen peroxide were Baker Analyzed Reagent Grade.

Acrylamide (Eastman Reagent Grade) and DMAEMA (Rohm & Haas; with 2000 ppm of MEHQ inhibitor) were used as received.

Diazyme L30 enzyme solution was from Miles Laboratories, Inc. Enzyme activity was not determined.

Graft Polymerization

Graft polymerizations were run with unmodified wheat starch and monomer systems that contained 0, 10, 20, 50, and 100 mole-% DMAEMA·HNO_3, the remaining monomer being acrylamide. The following procedure for a monomer mixture containing 20 mole-% DMAEMA·HNO_3 is presented as an example. A stirred slurry of 48.6 g (dry basis) of wheat starch [0.3 mole anhydroglucose unit (AGU)] in 390 ml of water was purged with a stream of nitrogen for 1 hr at 60°C to remove dissolved oxygen and then cooled to room temperature. For polymerizations onto unswollen starch, water was purged separately and then added to the starch. A mixture of 9.4 g (0.06 mole) of DMAEMA in 25 ml of nitrogen-purged water was acidified to pH 2 with 6*N* nitric acid (10 ml required), and 17.1 g (0.24 mole) of acrylamide was dissolved in the resulting solution. A solution of 0.12 g (3×10^{-4} moles) of ferrous ammonium sulfate hexahydrate in about 2 ml of water was added to the stirred starch slurry. After 5 min, the solution of monomers was added; and after an additional 5 min, addition of 0.35 g of 30% hydrogen peroxide (3×10^{-3} moles) in about 2 ml of water was made.

The mixture was stirred for 2 hr at 25°C and the reaction terminated by the addition of 2 g of hydroquinone. Since the amount of 6*N* nitric acid used depended on the mole percentage of DMAEMA·HNO_3 in the monomer mixture, the amount of water used to suspend the starch was adjusted in other reactions to keep the total water volume constant.

For graft polymerizations conducted in aqueous acetonitrile, 48.6 g of wheat starch was initimately mixed with a solution of 0.12 g of ferrous ammonium sulfate hexahydrate in 15 ml of water and the resulting mixture suspended in 150 ml of nitrogen-purged acetonitrile. A solution of acrylamide and DMAEMA·HNO_3 totaling 0.3 mole and 0.35 g of 30% hydrogen peroxide was prepared in a total of 260 ml of nitrogen-purged water and added to the starch slurry. The mixture was stirred for 2 hr at 25°C.

In all reactions, graft copolymers were isolated by centrifugation, extracted four times with cold water, and dried. Water extracts were dialyzed and freeze dried to give fractions that were largely ungrafted synthetic polymer. Carbohydrate contents of these fractions were on the order of 5–10%. Calculations for grafting efficiency were made as described previously.[2]

DMAEMA·HNO_3 Content of Polymeric Products

The mole percentages of DMAEMA·HNO_3 in both grafted and ungrafted synthetic polymers were calculated from the 100 MHz NMR spectra as determined in 5% or 10% D_2O solutions on a Varian HA-100 spectrometer. Signals at δ 2.88 (N-methyl groups of DMAEMA·HNO_3) and δ 1.66 (—CH_2— of polyacrylamide) were integrated, and the mole-% DMAEMA·HNO_3 was calculated from the following equation:

$$\text{mole-\% DMAEMA·HNO}_3 = \frac{(\text{integrated } \delta\ 2.88 \text{ signal} \div 6)\ (100)}{(\text{integrated } \delta\ 2.88 \text{ signal} \div 6) + (\text{integrated } \delta\ 1.66 \text{ signal} \div 2).}$$

The method was checked with known synthetic mixtures of polyacrylamide and poly(DMAEMA·HNO_3). The results in Table I are in agreement with theory at high mole percentages of acrylamide since the N-methyl signal of DMAEMA·HNO_3 is sharp and can be integrated accurately at low concentrations. The method is not useful, however, when acrylamide mole

TABLE I
Mole-% Poly(DMAEMA·HNO_3)[a] in Physical Mixtures with Polyacrylamide

Calculated	Found by NMR
50	46
21	22
9.1	9.1
3.9	3.9

[a] DMAEMA·HNO_3 = nitric acid salt of dimethylaminoethyl methacrylate.

percentages are much below 50% since the broad —CH_2— signal of the acrylamide repeating unit becomes obscured by baseline noise.

Hydrolysis of the Starch Moiety of Graft Copolymers and Molecular Weight of Grafted Synthetic Polymer

The weight-% grafted synthetic polymer in starch graft copolymers (% add-on) was calculated by two methods: gain in weight of starch after graft polymerization, and weight loss of the graft copolymer after removal of the starch moiety by depolymerization with enzyme or mineral acid.

Starch–poly(DMAEMA·HNO_3) graft copolymers, which contained no polyacrylamide, were heated under reflux in 0.5*N* hydrochloric acid, as previously described,[1] and the grafted branches were isolated from starch hydrolyzate by dialysis and freeze drying.

Graft copolymers that contained polyacrylamide were hydrolyzed enzymatically rather than in hot mineral acid, in which polyacrylamide tends to crosslink.[3] In 125 ml of water was suspended 10 g graft copolymer. The pH varied from 3.9 to 5.3. Slurries were heated on a steam bath to 90°C to swell and disperse the solid particles, the temperature was reduced to 60°C, and 1 ml of Diazyme L30 enzyme solution was added. Mixtures were stirred at 60°C for 7 hr, heated at 92–95°C for 15 min to destroy the enzyme, and then cooled to room temperature. When the polymer contained poly(DMAEMA·HNO_3), 2 g of sodium nitrate was added to ensure that acid salts of DMAEMA repeating units would be in the nitrate form. Reaction mixtures were dialyzed against distilled water and were then centrifuged to remove 0.1 to 0.3 g of insolubles. Grafted synthetic polymers, which contained less than 5% carbohydrate, were isolated from supernatants by freeze drying. In a separate experiment it was shown that the amount of enzyme contaminating the grafted polymer would be on the order of 20 mg.

Molecular weights were determined in 0.15*N* sodium chloride solution on a Melabs Model CSM-2 membrane osmometer equipped with a B-19 membrane (Schleicher and Schuell Co.). Control reactions established that the conditions of enzymic hydrolysis did not significantly change the molecular weights of either polyacrylamide ($\bar{M}_n$ 52,000) or a polyacrylamide–poly(DMAEMA·HNO_3) copolymer ($\bar{M}_n$ 42,000; isolated from a reaction in which amounts of the two monomers were equimolar).

Molecular weights for grafted polyacrylamide given here are higher than those reported earlier,[2] since the enzyme in the previous study did not remove carbohydrate completely during depolymerization of starch. Although it was then reasonably assumed that the remaining carbohydrate existed as endgroups on grafted polymer, we now know that a significant percentage of this carbohydrate was not bonded to synthetic polymer but was present as low molecular weight fragments, which lowered the observed $\bar{M}_n$.

The grafting frequency, expressed as the average number of AGU per grafted branch, was calculated from the per cent add-on and the molecular weight of grafted branches. Two grafting frequencies could be calculated,

depending on whether per cent add-on was determined by weight gain of starch or weight loss after starch depolymerization.

The influence of hydrolysis conditions on the mole-% DMAEMA·HNO_3 detected by NMR was determined by recording NMR spectra of a polyacrylamide–poly(DMAEMA·HNO_3) copolymer before and after it had been physically mixed with starch and treated with enzyme. The copolymer, synthesized in the absence of starch from a monomer mixture containing 20 mole-% DMAEMA·HNO_3, contained 22 mole-% DMAEMA·HNO_3 by NMR. After treatment with enzyme under the same conditions used with graft copolymers, NMR analysis showed 17 mole-% DMAEMA·HNO_3.

Flocculation

Slurries of graft copolymers (5 g in 800 ml of water; pH adjusted to 6) were heated on a steam bath (92–95°C) for 5 min and then dispersed by passing through a Penick & Ford laboratory-model continuous-steam-injection cooker[4] at 170°C and a steam pressure of 100 psi within the cooker. Portions of each dispersion were centrifuged for 20 min at 5000 × g and a portion of the clear supernatant was freeze dried. Per cent solubility was calculated from the weight of solid in the supernatant versus the weight of solid in a part of the uncentrifuged dispersion. Per cent solubility ranged from 90% to 95%. Solutions were acidified to pH 4 with nitric acid and diluted to a final concentration of 0.2 g/l.

Graft copolymers were tested as flocculants for Celite (a diatomaceous silica from Johns-Manville; average particle size 2.1 μ) as described previously.[5] The pH of Celite suspensions was 6.6–7.0.

RESULTS AND DISCUSSION

Synthesis and Characterization of Starch Graft Copolymers

Initiation of graft polymerization of mixtures of acrylamide and DMAEMA·HNO_3 onto unmodified wheat starch was with ferrous ammonium sulfate–hydrogen peroxide, since DMAEMA·HNO_3 will not graft-polymerize onto starch with ceric ammonium nitrate initiation.[1] Polymerizations run in totally aqueous media were carried out with both unswollen starch granules (starch slurried in water at 25°C) and starch swollen before the reaction by heating the water slurry for 1 hr at 60°C. Wheat starch granules swell and lose their birefringence on heating to 60°C; however, only about 2% of the solid is actually dissolved,[6] and graft polymerizations can still be viewed as taking place within an insoluble matrix.

Although polyacrylamide, poly(DMAEMA·HNO_3), and copolymers of the two monomers are water soluble, starch graft copolymers remain insoluble in cold water owing to the granule structure of starch. The graft copolymer can therefore be freed of unreacted monomer and ungrafted synthetic polymer by cold-water extraction, and the ungrafted

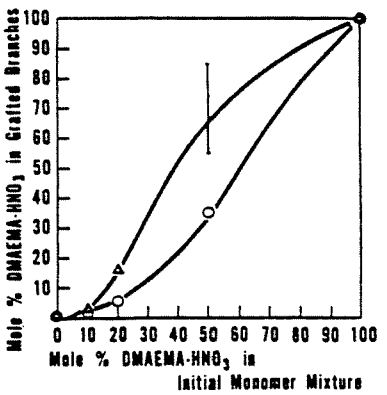


Fig. 1. Dependence of the composition of grafted polymer on the initial monomer mixture: (O) unswollen starch; (△) swollen starch. The vertical line at 50 mole-% indicates an approximate range due to the uncertainty of the analytical method (DMAEMA·HNO_3 = nitric acid salt of dimethylaminoethyl methacrylate).

polymer can be isolated by dialysis and freeze drying of the water extract. Water slurries of graft copolymers form smooth pastes when heated to near boiling, although the graft copolymers are not completely dissolved but are partially in the form of a highly swollen gel.

The products of graft polymerizations are shown in Table II, and the group of reactions run in water will be considered first. If we examine the DMAEMA·HNO_3 contents of isolated polymers, it is apparent that ungrafted polymers contain mole percentages of DMAEMA·HNO_3 which are equal to or greater than those in the initial monomer mixtures. Moreover, ungrafted polymers have a higher mole-% DMAEMA·HNO_3 when starch granules are unswollen. In contrast to ungrafted polymers, the mole-% DMAEMA·HNO_3 in grafted branches was less than that in the starting monomer mixture, with the exception of the reaction run with 50 mole-% DMAEMA·HNO_3 and swollen starch. At all monomer ratios examined, polymer grafted to swollen starch contained a higher percentage of DMAEMA·HNO_3 than polymer grafted to unswollen starch (Fig. 1).

The higher mole percentage of DMAEMA·HNO_3 in most ungrafted polymers than in the initial monomer mixture is not surprising in view of reactivity ratios calculated from published Q–e values for acrylamide[7] and two cationic monomers structurally similar to DMAEMA·HNO_3 [N,N,N-triethyl-N-(2-methacryloxyethyl) ammonium iodide[7] and the diethylaminoethyl methacrylate cation[8]]. As for the compositions of grafted branches, we can only speculate on possible reasons for our findings. A reduced rate of diffusion of DMAEMA·HNO_3 into the starch matrix, relative to acrylamide, would explain the low DMAEMA·HNO_3 content of grafted polymer, and such a reduced diffusion rate might reasonably be caused by electrostatic repulsion by initially grafted cationic monomer. The higher DMAEMA·HNO_3 content of grafted polymer at 50 mole-% cationic monomer could then be due to a suppression of this repulsion by

TABLE II
Products of Graft Polymerization

Starting material		Graft copolymer						Ungrafted polymer		
		% Add-on[a]		Grafted branches		AGU[b]/graft				
DMAEMA·HNO$_3$, mole-%	Starch pretreatment temp., °C	Weight gain	Weight loss	$\bar{M}_n$	DMAEMA·HNO$_3$, mole-%	Weight gain	Weight loss	$\bar{M}_n$	DMAEMA·HNO$_3$, mole-%	Grafting efficiency,[c] %
Reactions Run in Water										
0	25	18	16	81,000	0	2300	2600	50,000	0	53
0	60	12	13	252,000	0	11,400	10,400	52,000	0	34
10	25	17	13	126,000	1.7	3800	5200	35,000	13	41
10	60	13	14	250,000	2.5	10,300	9500	38,000	11	33
20	25	13	9	87,000	5.8	3600	5400	29,000	32	30
20	60	11	13	126,000	16	6300	5200	41,000	21	26
50	25	9	9	148,000	35	9200	9200	47,000	>50	21
50	60	9	10	55,000	>50	3400	3000	35,000	>50	20
100	25	12	12	567,000	100	25,700	25,700	46,000	100	17
100	60	17	19	87,000	100	2600	2300	44,000	100	25
Reactions Run in Acetonitrile–Water										
20	25	10	7	76,000	1.8	4200	6300	24,000	>50	30
50	25	16	11	66,000	14	2200	3300	25,000	>50	42

[a] Weight gain: per cent add-on determined by gain in weight of starch after graft polymerization. Weight loss: per cent add-on determined by loss in weight of graft copolymer after depolymerization of the starch moiety with enzyme or mineral acid.

[b] Anhydroglucose unit.

[c] Percentage of total polymer formed in a reaction that is grafted to starch.

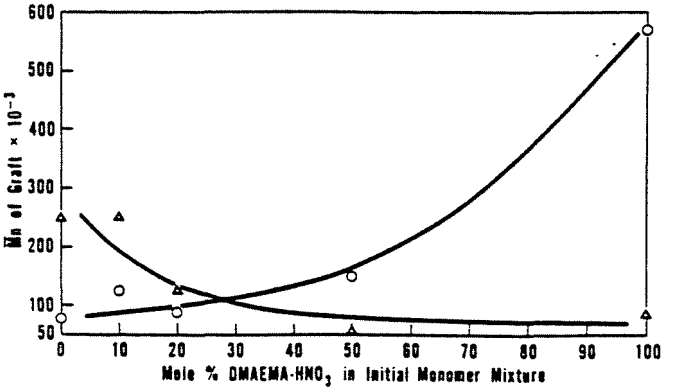


Fig. 2. Dependence of $\bar{M}_n$ of grafted polymer on the composition of the initial monomer mixture: (○) unswollen starch; (△) swollen starch.

the higher ionic strength of the aqueous medium. Moreover, the repulsion of DMAEMA·HNO_3 by a given number of cationic substituents per starch granule should diminish as the volume of the swollen granule matrix increases. This would account for the increased incorporation of DMAEMA·HNO_3 in polymer grafted onto swollen starch.

Let us now examine the influence of starch granule swelling on the molecular weight and frequency of grafted branches for the reactions in Table II run in water. Swelling the starch granules at 60°C with acrylamide as the monomer produces longer and less frequently grafted branches as compared with unswollen starch; whereas increased granule swelling gives shorter and more frequent grafts with DMAEMA·HNO_3. Since increased starch granule swelling has the opposite effect on $\bar{M}_n$ and frequency of grafts with acrylamide and DMAEMA·HNO_3, the mixed monomer systems were of particular interest.

In Figures 2 and 3, $\bar{M}_n$ of grafted polymer and grafting frequency for both swollen and unswollen starches are plotted against mole-% DMAEMA·HNO_3 in the initial monomer mixtures. In Figure 3, most grafting frequencies are indicated as ranges rather than as single points, since values for per cent add-on used in the grafting frequency calculations differ, depending on whether they were determined by weight gain or weight loss. For both grafting frequency (Fig. 3) and $\bar{M}_n$ of grafted polymer (Fig. 2), the curves for swollen and unswollen starches cross at about 25–30 mole-% DMAEMA·HNO_3. At this cationic monomer content, the influence of granule swelling on graft copolymer structure is minimal. At lower cationic monomer contents, the grafting behavior for swollen versus unswollen starch resembles that of acrylamide, while at higher DMAEMA·HNO_3 contents results become more analogous to DMAEMA·HNO_3 itself. At 25–30 mole-% DMAEMA·HNO_3 in the initial monomer mixture, the DMAEMA·HNO_3 content of grafted polymer would be about 10 and 30 mole-% for unswollen and swollen starch, respectively, as estimated from Figure 1.

Grafting efficiencies, expressed as the percentage of the total polymer formed in a reaction that is actually grafted to starch,[2] were low since appreciable amounts of ungrafted synthetic polymer were formed. Grafting efficiencies for the series of reactions run in water decreased as the mole-% DMAEMA·HNO_3 in the monomer mixture increased. For all polymerizations, the $\bar{M}_n$ of ungrafted polymer was less than that of grafted polymer.

In the last two reactions of Table II, an acetonitrile–water solvent system was used, similar to that described earlier.[1] In these reactions, starch was first intimately mixed with ferrous ammonium sulfate hexahydrate, which had been dissolved in a small volume of water. The

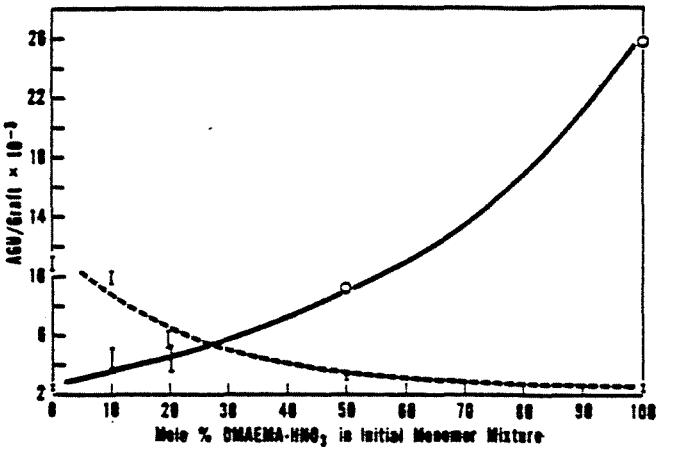


Fig. 3. Dependence of grafting frequency on the composition of the initial monomer mixture: (——) unswollen starch; (- - - - -) swollen starch. Vertical lines indicate variations in grafting frequencies that result from differences between per cent add-on by weight gain and by weight loss (AGU = anhydroglucose unit).

treated starch, which still retained its dry appearance, was next suspended in acetonitrile, and graft polymerization was initiated by addition of a combined water solution of DMAEMA·HNO_3, acrylamide, and hydrogen peroxide. Since acetonitrile is miscible with water but does not dissolve ferrous ammonium sulfate, a high concentration of ferrous salt is maintained within the starch matrix until such time as the water solution of monomers and peroxide is added.

When graft copolymers prepared in acetonitrile–water were compared with those prepared in water alone, large differences were observed in the compositions of the synthetic polymers. In acetonitrile–water, grafted branches contained less DMAEMA·HNO_3 than the polymers from corresponding reactions run in water. The efficiency with respect to utilization of cationic monomer is therefore drastically reduced by graft polymerization in acetonitrile–water.

Laboratory Testing as Flocculants

Although graft copolymers could be dispersed in hot water to give smooth pastes, a significant amount of insoluble polymer remained as a highly swollen gel when dispersions were diluted to the concentrations required for flocculation testing. Hot dimethyl sulfoxide followed by exhaustive dialysis, a method used successfully by us previously[1] to dissolve starch–DMAEMA·HNO_3 copolymers in water, also failed to dissolve the acrylamide–DMAEMA·HNO_3 graft copolymers completely.

Starch graft copolymers were finally dissolved by passing them through a laboratory-model steam-jet cooker. As we reported earlier,[1] this method of solution preparation reduces the molecular weight of the starch backbone and also the grafted branches, if these are of high molecular weight. For example, the intrinsic viscosity of a sample of unmodified wheat starch was reduced from 1.6 to 0.8 dl/g by jet cooking. Similarly, the $\bar{M}_n$ of grafted branches in a sample of starch–DMAEMA·HNO_3 graft copolymer was reduced from 230,000 to 136,000. Since these molecular weight reductions are probably caused by a mechanical rupturing of carbon–carbon bonds due to the instant swelling and disruption of the starch granule matrix, we reasoned that lower molecular weight grafted branches would probably not be so subject to this type of shear degradation. When we jet cooked a sample of the graft copolymer in Table II prepared from swollen starch and 100% DMAEMA·HNO_3, the $\bar{M}_n$ of grafted polymer indeed remained unchanged at 87,000.

The flocculation of 3% aqueous suspensions of Celite with selected graft copolymers is shown in Table III. The graft copolymer prepared from unswollen starch and acrylamide is not included since this product was incompletely dissolved by jet cooking. Graft copolymers with high molecular weight grafts are also excluded since grafted branches in these products are subject to severe shear degradation. Both the per cent add-on of the graft copolymer and the mole-% DMAEMA·HNO_3 in the grafted branches undoubtedly are factors in determining the efficiency of graft copolymers as

TABLE III
Flocculation of Celite

Graft copolymer						
	Grafted branches		Celite remaining in suspension at different concns. of graft copolymer, %			
% Add-on (weight gain)	$\bar{M}_n$	DMAEMA·HNO_3, mole-%	0 ppm	4 ppm	8 ppm	12 ppm
17	126,000	1.7	88	80	64	35
13	87,000	5.8	87	86	66	48
11	126,000	16	86	74	61	41
9	148,000	35	86	72	51	44
9	55,000	> 50	86	76	56	47
17	87,000	100	86	66	41	28

flocculants. None of the polyacrylamide-containing graft copolymers tested was as effective as the product prepared from DMAEMA·HNO_3 alone. It is apparent from the first and last entries, where graft copolymers have the same per cent add-on, that more than about 2 mole-% DMAEMA·HNO_3 is needed in grafted branches for good flocculating efficiency, especially at lower concentrations of flocculant. The large difference between the last two polymers in the table is probably because the per cent add-on in the acrylamide-containing copolymer was low.

We are indebted to Dr. D. Weisleder for NMR spectra and also for his advice about the NMR determination of DMAEMA·HNO_3 in polymeric products. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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Received March 3,1972